

**REMARKS**

Claims 1 and 2 are amended herein. Claims 3-16 are withdrawn from consideration.

Claims 17-23 are added as new claims. Support for the new claims is found, for example, in the specification on page 6, lines 13-20, page 7, line 14 to page 8, line 2, page 8, lines 3-11 and page 46, line 14 to page 47, line 12. Hence no issues of new matter are presented.

Accordingly, upon entry of the Amendment, claims 1-23 will be all of the claims pending in the application.

**I. Restriction**

Applicants respectfully request rejoinder of the non-elected claims, claims 3-16, if claims 1 and 2 are found allowable.

**II. Priority**

The Examiner has acknowledged Applicants' claim for foreign priority and receipt of some of the certified copies of the priority documents.

The Examiner indicates that certified translations of priority documents JP 2001-310289 filed on October 5, 2000, JP 2001-102468 filed on March 30, 2001, JP 2001-078191 filed on March 19, 2001, and JP 2001-397237 filed on December 27, 2003 have not been provided.

Applicants respectfully submit that "certified translations of the priority documents" are not required to perfect Applicants' claim to foreign priority. However, "certified copies of the priority documents" are required. In this regard, certified copies of the above-mentioned priority documents were in fact submitted in the present application on February 1, 2002.

Further, as indicated in the Petition Pursuant to 37 C.F.R. § 1.59 and MPEP § 724.05 to Expunge Copies of Papers from Application File, submitted on December 10, 2003, certified copies of priority documents JP 2001-0008000 and JP2001-374801 were inadvertently filed in this application and were intended for another copending application.

In view thereof, Applicants respectfully request confirmation of receipt of the certified copies of priority documents JP 2001-310289, JP 2001-102468, JP 2001-078191, and JP 2001-397237 in the present application.

Further, Applicants respectfully request return of the certified priority documents JP 2001-0008000 and JP2001-374801 for filing in the proper application pursuant to the Petition filed on December 10, 2003.

### **III. Response to Rejections Under 35 U.S.C. § 112, second paragraph**

Claims 1 and 2 are rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which Applicant regards as the invention.

Specifically, the Examiner states that in claim 1, the identifier “a” is missing before the word “covalent”. Further, the Examiner asserts that the phrase “introduction amount” is indefinite in because it insinuates that the current stated amount of compound B used in the reaction is a beginning amount. The Examiner states that if this is the case, the amount stated would be the lower end of the amount of compound B required to perform the modification of gelatin and the question remains as to what is the upper end of the amount of compound B that is required to perform the modification reaction.

Claim 1 is amended to recite “a covalent bond”, thereby obviating this ground for rejection.

Claims 1 and 2 are further amended to delete the term “introduction” to clarify the claim language. In the present invention, the amount of the compound added in the reaction is widely different from the amount of the compound which actually reacts with the reactive group in the gelatin and taken in the gelatin to form a covalent bond.

Accordingly, Applicants respectfully request withdrawal of the rejection.

#### **IV. Response to Rejections Under 35 U.S.C. § 101**

Claims 1 and 2 are rejected under 35 U.S.C. § 101 as allegedly being directed to non-statutory subject matter.

The Examiner states that the peptide of the invention resembles naturally occurring gelatin and therefore does not constitute patentable subject matter. The Examiner states that amending the claims to recite “isolated or purified” peptide would overcome the rejection.

Applicants traverse the rejection and submit the following.

The term “gelatin” in the broad sense is a generic term used to refer to substances having a peptide bond. Gelatin, including naturally occurring gelatin, does not contain any compound which contains a nitrogenous ring having a mercapto group as in the independent claims of the present application. Such a compound is not mixed as an impurity into gelatin either. This is clear from the attached reference article, “The Theory of the Photographic Process”, 4<sup>th</sup> Ed., T. H. James, Ed., p. 67-70, Macmillan, New York (1977). See Attachment.

Further, the independent claims of the present application recite a “modified gelatin” and not a “gelatin”. In addition, claim 1 clearly recites that the modified gelatin is obtained by reacting “a gelatin” with a “compound which contains a nitrogenous aromatic ring having a mercapto group to form a covalent bond with a reactive group in the gelatin.” Thus, the claims clearly recite that the claimed gelatin is an artificially modified gelatin. Thus, the claimed modified gelatin can be clearly distinguished from naturally occurring gelatin. New claims 21-23 are directed to an isolated and purified gelatin as suggested by the Examiner.

Accordingly, Applicants respectfully request withdrawal of the rejection.

**V. Response to Rejections Under 35 U.S.C. § 102(b)**

Claims 1 and 2 are rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by Miyake (U.S. Patent No. 5,362,601).

According to the Examiner, Miyake discloses a composition that is obtained by reacting gelatin and a compound that contains a nitrogenous aromatic ring having a mercapto group and the amount of the compound used is between  $1.1 \times 10^{-6}$  mol to  $1.1 \times 10^{-3}$  mol per 100g of gelatin and therefore Miyake anticipates the claimed invention.

Applicants respectfully traverse the rejection and submit that Miyake neither discloses nor suggests the presently claimed invention.

Specifically, none of emulsions (1)-(3) of Miyake uses the modified gelatin recited in the present claims. For example, although Miyake discloses a method of preparing emulsion (1) in column 22, lines 11-55, the gelatin used in the method is a simple “gelatin” having no particular feature, and not the modified gelatin of the present invention. Further, Compound A used in

preparation of the emulsion (1) in Miyake does not have a mercapto group (-SH) as in the present invention. Instead Compound A has a thioxo group (=S). Even further, Compound A of Miyake is a heterocyclic compound containing a nitrogenous ring, but the ring is not an aromatic ring and the compound does not have any reactive group that reacts with gelatin. It is obvious not only those skilled in the art but also to those having knowledge of organic synthesis that Compound A of Miyake and gelatin do not react with each other to form a covalent bond, under the emulsion preparation conditions (for example, pH 6.1, at 60°C, etc.) described in the method of emulsion (1). Thus, Miyake does not teach all elements of the claimed invention and does not anticipate the claimed invention.

In addition, as shown in Table 3 in column 24 of Miyake, the mercapto compounds (1)-(3) (columns 27-28) are used in the 1st layer, 3rd layer, and 5th layer. In the mercapto compound (1), the mercapto group is a substituent in a benzene ring, not a nitrogenous aromatic ring, and in the mercapto compounds (2) and (3), the mercapto group is a substituent in a nitrogenous aromatic ring; however, they do not react with gelatin. Specifically, for example, the >NH group in the benzoimidazole ring of the mercapto compound (2), and -NHC(=O)NHCH<sub>3</sub> in the mercapto compound (3) do not react with gelatin, unless they are put under such hostile conditions that the silver halide emulsion is decomposed. The same is applicable to the mercapto group. The mercapto compounds (1)-(3) are used for at least preventing fog of silver halide emulsion, and they exert their effects by reaction between the mercapto group and silver. If the mercapto group itself reacts with gelatin in Miyake, Miyake cannot achieve the effect of preventing fog.

Therefore, Miyake does not anticipate nor render obvious the modified gelatin of the present claimed invention.

**VI. Conclusion**

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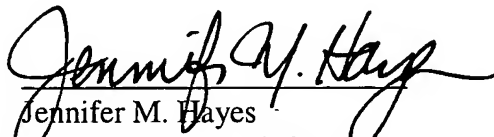
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Date: June 14, 2004

THE  
THEORY  
OF THE  
PHOTOGRAPHIC  
PROCESS  
FOURTH EDITION

Macmillan Publishing Co., Inc.

NEW YORK

Collier Macmillan Publishers

LONDON

ATTACHMENT

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PRINTED IN THE UNITED STATES OF AMERICA

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Macmillan Publishing Co., Inc.  
866 Third Avenue, New York, New York 10022

Collier Macmillan Canada, Ltd.

Library of Congress Cataloging in Publication Data

Main entry under title:

The Theory of the photographic process.

First and 2nd editions edited by C. E. K. Mees.

Includes bibliographical references and indexes.

1. Photography. I. James, Thomas Howard, (date)

II. Mees, Charles Edward Kenneth, 1882-1960. The theory of the photographic process.

TR200.M4 1977 770 76-25432  
ISBN 0-02-360190-6

PRINTING 3 4 5 6 7 8 YEAR: 3

ISBN 0-02-360190-6



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## II. PROPERTIES OF GELATIN IN RELATION TO ITS USE IN THE PREPARATION OF PHOTOGRAPHIC EMULSIONS

### J. POURADIER

THE PHOTOGRAPHIC activity of a gelatin depends more on the substances associated with it than on the protein molecule itself. The free groups of the molecule have some influence, but the action of gelatin is due chiefly to the foreign substances it contains.

For many years, the gelatin was used as manufactured and contained substances essential for sensitization. This was the era of active gelatins, when gelatin had to contain the correct amounts of all the active microcomponents. This empirical technology produced excellent results, but little by little it was recognized that it would be preferable to have the gelatin act only as a binding agent and to add to it, at the right time, controlled amounts of the necessary substances. We thus reached the era of "inert" gelatin, in which, by using proper procedures, most of the active sulfur or reducing components contained in the raw materials were removed. It should be noted that this does not mean that inert gelatin is totally "empty"; for in spite of improvements in manufacturing techniques, the purification is never complete and all gelatins, even the purest ones, contain photographically active substances such as restrainers and reducers. These substances are quite numerous,<sup>1</sup> even in inert gelatins. We shall consider the main ones under classifications assigned arbitrarily according to the chemical characteristics that seem to be the most important photographically.

#### A. Microcomponents of Gelatin

##### 1. INORGANIC SALTS

Gelatins that have not been treated to demineralize them contain inorganic salts. Certain of these salts, such as alkali and alkaline earth phosphates, silicates, and sulfates, have limited photographic influence,

which is manifest only at high concentrations. The soluble calcium salts, which retard chemical sensitization,<sup>2</sup> provide an example of this behavior.

Other salts, usually present in smaller quantities, have more pronounced effects. Among these are (1) nitrites, usually produced by bacterial reduction of nitrates; (2) sulfites, produced in part from the partial oxidation of sulfur containing constituents of the raw material and partly from the sulfur dioxide added to decolorize the gelatin and destroy the aerobic bacteria; (3) salts of the heavy metals (Cu, Fe, Hg, . . .) which are rather troublesome even at low doses; (4) chlorides, which, although they form a more soluble salt of silver than bromide or iodide, influence the precipitation of the other halides and modify the crystal dimensions,<sup>3</sup> and (5) thiosulfate and thionates.

##### 2. SULFUR-CONTAINING COMPONENTS

Atoms of sulfur in compounds, such as thiosulfate or thiourea, that modify the properties of the photosensitive crystals during the preparation of the emulsions (Chapter 5, Section I) are considered as labile or active in contrast to the sulfur of other materials, such as sulfate, that are inactive under the same conditions. Thus, depending upon their behavior with respect to the photographic crystal, the usual practice is to distinguish between active or labile sulfur and inert sulfur, the former being technologically the more important.

It is generally assumed that the principal source of photographically active sulfur in gelatin is the cystine of the proteins accompanying the collagen in the raw materials. This amino acid is profoundly modified in the course of preparation of the gelatin, but the reactions are incomplete and a part remains in the final product. Thus, from a commercial gelatin extracted from limed hides, Maron<sup>4</sup> isolated by adsorption on

active carbon a protein rich in cystine. Mucoproteins containing cystine have also been found in hide and bone gelatins, whether treated with lime or with acid.<sup>5</sup>

The quite general presence of cystine in photographic gelatin does not obviate the possibility that a substantial proportion of the cystine of the primitive material has disappeared or been transformed during extraction. The transformations, followed or not by the elimination of the sulfur containing compounds, are very complex, consisting of several decomposition and redox reactions that occur either simultaneously or successively. In the presence of strong bases, either soda or lime, cystine forms sulfide and polysulfides which, in contact with air, are oxidized to sulfite and sulfur.

These chemicals react together to give thiosulfate which, in turn, can be oxidized to polythionates. Thiosulfate and several other substances carrying active sulfur atoms have been detected by electrophoretic analysis<sup>6</sup> in aqueous solutions of limed cystine and the complexity of the overall reactions involved is such that molecules as elaborate as 2-methylthiazolidine-2,4-dicarboxylic acid are synthesized.<sup>7</sup> In the presence of gelatin, the reactions are still more complicated since the products interact with the other constituents and give substances of very different composition. The presence of thiosulfate in photographic gelatins was suggested in 1928 by Steigmann and has been proved experimentally by Wood<sup>8</sup> and confirmed many times since. In contrast, the presence of tetrathionate has never been satisfactorily demonstrated. Although Wood<sup>8,9</sup> and Russell<sup>10</sup> reported detection of this material in various photographic gelatins, Beersmans and Borginon<sup>11</sup> believe that it resulted from the partial decomposition during the analysis of thiosulfate contained in the gelatins examined. Moreover Nellist<sup>12</sup> has shown that tetrathionate cannot exist in the presence of sulfur dioxide, with which it reacts to give thiosulfate and trithionate. This conclusion is confirmed by the influence of pH on the gelatin-silver nitrate reaction: almost all the active gelatins respond as would thiosulfate to the pH variation.<sup>13</sup>

Nevertheless a few gelatins behave differently and their responses are intermediate between that of thiosulfate and that of tetrathionate. This observation does not imply that these gelatins contain a mixture of the two compounds but shows that one of their microcomponents behaves like tetrathionate in the presence of silver nitrate.<sup>13</sup>

The simultaneous formation of trithionate and thiosulfate caused by sulfur dioxide supports the suggestion of Steigmann concerning the existence of trithionate in photographic gelatin, and it is possible that the repeated failures<sup>6,9</sup> to detect this chemical are due to its high instability.

Cystine, thiosulfate, and thionates are not the only active sulfur components of gelatin. Several other substances have also been found; among them thiourea and its derivatives deserve special attention for, although it is certain that a microcomponent of gelatins, particularly of pigskin gelatins,<sup>14</sup> behaves like thiourea in the presence of ammoniacal silver nitrate, this material has never been isolated from gelatin, and all conclusions concerning its composition are subject to discussion.

The elimination of active substances contained in the raw materials is time consuming and difficult. A part of these substances remain in finished gelatin and, in order to complete their elimination, several treatments have been tried. The simplest technique seemed to be their destruction by oxidation; many patents claim the use of peroxides but, unfortunately, the results obtained have not always matched the hopes. Nitric acid added to the deliming baths partially oxidizes the sulfur components and facilitates their elimination.<sup>15</sup> Recently, efforts were made by some manufacturers to reduce the impurity levels in their gelatins by using new techniques of preparation; extraction of soluble collagen followed by denaturation at high temperature seems to be a promising technique.<sup>16</sup>

In addition to their natural components, photographic gelatins may contain synthetic materials added during the preparation to provide particular properties.<sup>17,17</sup>

The low concentration of the sulfur containing substances in gelatins considerably complicates their identification and determination, and many analytical techniques have been proposed.

The Feigl reaction uses the catalytic action of sulfur components on the decomposition of sodium azide in the presence of iodine. The volume of nitrogen released depends upon the sulfhydryl, disulfide, thiosulfate, and thionate groups, but equivalent amounts of these substances do not yield the same volume of nitrogen. This inconvenience is partially offset by the substantial advantages resulting from the sensitivity and the simplicity of the method, which generally provides results in rather good agreement with the photographic properties of the gelatins analyzed.

Filtering the gelatin solution before analysis sometimes causes significant diminution in the volume of nitrogen liberated.<sup>18</sup> This behavior shows that these gelatins contain dispersed particles that have a catalytic action, either because they contain sulfur compounds or because they are surface active.

In the technique of Abribat,<sup>19</sup> derived from that of Sheppard and Hudson, the labile sulfur of the gelatins reacts with ammoniacal silver nitrate, the excess being

measured potentiometrically. As described, this procedure does not eliminate completely reaction with reducing substances and, for certain gelatins, overestimates the labile sulfur content. A modification of the experimental procedure allows the elimination, or at least a considerable reduction, of these interferences.<sup>20</sup> Abribat's method offers a number of advantages and, being multifunctional, allows a differentiation to be made between the active components by the change in order of introduction of the reagents and by operation at various temperatures. Thus, it is possible to measure separately thiourea and its derivatives by adding the ammoniacal solution before the silver nitrate and omitting the digestion.<sup>14</sup> The thiosulfate, which does not react with the silver ions in the presence of a large excess of ammonia, is not measured normally by Abribat's technique, but it may be measured if the gelatin is kept for a few minutes at 60–80°C in the presence of silver bromide<sup>21</sup> or silver nitrate free of ammonia.<sup>14,22</sup>

The thiosulfate in gelatin may also be determined by controlled oxidation after it has been isolated by an ion exchange resin<sup>23</sup> or by polarography with<sup>10,24</sup> or without extraction.<sup>25</sup> In this case, the response depends upon the viscosity of the solution, and it is necessary to make a standardization for each gelatin or to degrade the protein by the addition of trypsin before the polarographic measurements.<sup>26</sup> Warburton and Przybylowicz<sup>27</sup> have described a colorimetric method based on reduction of thiosulfate to sulfide and subsequent formation of methylene blue. This method gives results in good agreement with those obtained by direct polarography.

In addition to these specific techniques, more general methods exist in which no attempt is made to determine the individual components but all the substances having a common functional group or similar behavior are considered together. For instance, it has been proposed to evaluate the overall labile sulfur content by reaction of the gelatin with a mixed silver and mercury oxalate precipitate<sup>28</sup> and Titov and Ratner<sup>29</sup> have shown that the photographically active substances may be measured by following the reaction of the gelatin with increasing quantities of silver nitrate. This last method was subsequently simplified by Karpova,<sup>30</sup> who selected three experimental conditions to distinguish between restrainers, sulfiding agents, and complexing agents. A systematic study by Nellist and Janus<sup>31</sup> defined the nature of the components reacting at each stage of the titration.

### 3. OSES AND POLYOSES

The principal carbohydrates associated with mammalian collagen are

1. Polysaccharides, mucopolysaccharides, polyuronic acids, hyaluronic acids, and chondroitin sulfate. They give by hydrolysis neutral sugars (fucose, mannose, glucose, galactose), amino sugars (glucosamine, galactosamine) and uronic acids (glucuronic acid, galacturonic acid).
2. Sialic acids,<sup>32</sup> principally *n*-acetylneuraminic acid, present at 50–300 ppm.
3. Nucleic acids (ribose and deoxyribose).

The carbohydrates of the original raw material are partially decomposed and eliminated during the gelatin preparation, principally by the acid and alkaline solutions. When the degradation is sufficient, the products diffuse in the swollen collagen and dissolve in the treatment baths, which carry away a quantity with each replacement.<sup>33</sup> The elimination of the carbohydrates is never complete and, besides a few degraded substances, the sugars found in commercial gelatins are galactose and glucose (the latter in smaller quantities),<sup>34</sup> the hexosamines<sup>35</sup> and polyhexosamines,<sup>36</sup> the uronides,<sup>35–37</sup> ribose and deoxyribose.<sup>38</sup> Part of these sugars is free and reacts easily, but the rest is more or less tightly bound and must be freed by preliminary hydrolysis before it can react.<sup>37</sup>

### 4. ALDEHYDES AND PRECURSORS OF ALDEHYDES

Steigmann suggested that aldehydes are present in gelatin, and tried to reveal them *in situ* by the use of color reactions. All the analysts who have continued his investigation used the same technique since it has not been possible, up to the present, to isolate the substances sought nor to reach them by another path.

Three reagents are utilized currently: thiobarbituric acid (TBA), 3-methyl-2-benzothiazolone hydrazone chlorhydrate (MBTH),<sup>39</sup> and 2,3,5-triphenyltetrazolium chloride (TTC). These reagents do not detect the same aldehydes, and their reactivities are strongly influenced by certain constituents of the gelatins, which, depending upon the case, interfere with or enhance the formation of dye.<sup>40</sup>

A study<sup>41</sup> of the dyes formed has shown that the reaction of gelatins with TBA depends upon the presence of glyceric aldehyde, pyruvic aldehyde (methylglyoxal), dihydroxyacetone, malonic aldehyde, and 5-hydroxymethylfurfural, to which it is probably advisable to add pyruvic acid.<sup>37</sup> These carbonyl components may preexist in a free or combined state in the gelatin under analysis or may have been created in the course of the analysis and result from the decomposition of constituents of the gelatin during analysis.

The constituents that react as aldehyde in the color reactions, but are not aldehydes by themselves, have been called aldehyde precursors.<sup>41</sup> They belong to

chemically varied groups, the principal ones being the oses<sup>42</sup> and the enediols that are derived by alkaline treatment, the peroxides formed from the unsaturated fatty acids, and the nucleic acids.<sup>43a</sup>

It is difficult at the present time to specify the amount of the aldehydes in what is usually called the aldehyde content of gelatins, but several observations seem to show that the precursors are, if not the only, at least the principal, substances responsible for the color reactions of gelatins.<sup>43</sup>

#### 5. NUCLEIC ACIDS

The term **nucleic acid** designates two classes of materials: ribonucleic acid (RNA) and deoxyribonucleic acid (DNA). These acids are made up of (1) sugars: ribose (RNA) and deoxyribose (DNA); (2) purine or pyrimidine bases: adenine, guanine, cytosine (RNA and DNA), uracyl (RNA), and thymine (DNA); and (3) phosphate groups.

In addition to the differences between RNA and DNA, in each class substantial variations in composition exist, the proportions of the different constituents depending on the origin of the sample under examination.<sup>43b</sup>

The nucleic acids associated with the raw material used for the preparation of the gelatins are substances with molecular weights of the order of millions. They are easily split into smaller molecules called nucleotides and undergo substantial degradation during the preparation of the gelatins.<sup>44</sup> Their stability depends on their composition, and it has been shown that the alkaline pretreatments destroy more of the RNA than of DNA.<sup>30b</sup> The degradations are generally limited to nucleotides, but they may sometimes free the mononucleotides (base, sugar, and phosphate group) and even the nucleosides (base and sugar). Thus, the content of nucleic acids and of their derivatives in gelatin depends upon both the raw materials used and the technique of preparation, and seldom exceeds  $2 \text{ mg g}^{-1}$ , approximately  $200 \mu\text{g}$  of adenine per gram. DNA is generally more abundant than RNA in photographic gelatins, but exceptions to this rule frequently result from special treatments.<sup>38</sup> Nucleic acids can be determined by their three constituents, which can be measured *in situ* or after having been extracted from the gelatin.<sup>38a,b,45</sup>

The restraining properties of the nucleic derivatives depend upon their degree of depolymerization.<sup>36,46</sup> The determination of this parameter implies the ability to extract the nucleic derivatives from the gelatins without altering them. Some encouraging results in this direction have already been obtained by concentrating the products studied by coacervation with alcohol<sup>47</sup> or by fixing them on ion exchange resins.<sup>44</sup>

### B. Interactions of Gelatin

#### 1. THE REDUCING POWER OF GELATIN

Owing to their differences in composition, the reducing substances of gelatins (aldehydes and precursors, oses, polyoses, uronides, amino-sugars, methionine, sulfite, nitrite, and so on) have very widely divergent properties, and whereas some of them need strong oxidants to react, others are able to reduce much less active materials. Under these conditions the concentration of efficient reducers is a function of the reactivity of the oxidant used: the higher the activity of the oxidant used for the determinations, the higher are the values obtained for the reducing power of gelatin.

The most commonly employed oxidants are silver nitrate (which is utilized for the measure of the Vogel value), iodine,<sup>48</sup> ferricyanide,<sup>49</sup> potassium chromate,<sup>37a</sup> and auric salts.<sup>50</sup> The last often results in the highest measures of the reducing power.

Moreover, the influence of the reaction time must not be underestimated since certain substances that react very slowly and are not detected by a quick titration have a significant action during a prolonged reaction. Under these conditions the measurement of "reducing power" has meaning only if all the experimental conditions are specified.

#### 2. THE INTERACTION OF GELATIN WITH SILVER AND NOBLE METAL IONS

The sensitization of photographic emulsions is frequently carried out with salts of noble metals, and their action depends, to a large extent, upon their reactivity with gelatin. The reactions of the noble metal ions and those of silver ions with gelatin depend on the same properties of gelatin and its impurities. Studies have shown that several successive or simultaneous reactions can occur, which are conditioned by many parameters, the principal ones being the pH, the temperature, and the metal ion/gelatin ratio. The role of this last variable is very important because certain constituents of the gelatin behave differently, depending upon the concentration of the free metal ions present. For example, the thiosulfate in active gelatins associates reversibly with silver ions when the concentration of these ions is low but disproportionates irreversibly at higher concentration. Thus, we observe the formation of the soluble argentomonothiosulfate complex in the first case and the precipitation of silver sulfide in the second. This duality of behavior explains why progressive titration by careful addition of a solution of a noble metal salt does not give the same result as a back titration carried out after the addition of a large excess of reagent.